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FR-A- 972 178 GB-A- 1 411 010
GB-A- 2 127 393 US-A- 3 567 433
US-A- 3 953 200 US-A- 4 145 397
US-A- 4 382 068 US-A- 4 409 190
US-A- 4 514 368

International Dictionary of Metallurgy - Min-
eralogy - Geology, Page 523, Technoprint
International, Milano, Italy 1970

Ernst, Dictionnaire General de la Technique
Industrielle, page 414, Vol. 4, Brandstetter
Verlag, Wiesbaden, BRD, 1988

Harrap's shorter, French-English and
Anglais-Français, page 253, Harrap Limited,
London, GB, 1982

De Vries, French-English Science and Tech-
nology Dictionary, 4th Edition, page 173

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Description

This invention relates to methods of leaching metals from metal-containing particles, such as spent hydroprocessing catalysts.

5 One modern development in crude oil processing is the upgrading of metal- and sulfur-containing feedstocks (e.g., crude oils and residua) by hydroprocessing methods. Such upgrading is necessary to convert the heavy feedstock into more valuable, lower boiling fractions and to remove metals and sulfur contaminants that can pollute the atmosphere upon combustion.

Crude oils contain various dissolved contaminants, including nickel, vanadium, iron, and sulfur. The 10 lighter fractions are frequently distilled off under either atmospheric pressure or a partial vacuum, leaving the metals in a high boiling fraction called the "residua." Residua will generally contain at least 35 ppm metal contaminants, frequently as high as 100 ppm, and in extreme cases, higher than 1000 ppm.

These metals, and any sulfur present, are removed by processing the feedstock with a catalyst in the presence of hydrogen. Such catalysts are generally a solid support that contains catalytic metals, generally 15 a Group VIII metal alone or in conjunction with a Group VI metal. The Group VI metal is typically tungsten or molybdenum and the Group III metal is typically nickel or cobalt. As the catalyst is used, metals from the feedstock deposit on its exterior surface and the interior surface of its pores, eventually plugging the pores and reducing the activity of the catalyst to such an extent it does not give the desired product quality. Such catalysts are herein defined as "spent catalysts," and contain catalytic metals, an inorganic support matrix, 20 metals removed from the feedstock, sulfur compounds, and a hydrocarbonaceous residuum.

Recently, the obtainable crude oil is tending to be heavier, forcing refiners to use more hydroprocessing catalysts than heretofore necessary to remove metals and sulfur from the feedstock. It is therefore possible that a shortage will develop of the valuable catalytic metals, particularly cobalt. Efforts have been made to extract metals from hydroprocessing catalysts so that the catalytic metals, the deposited metals, and the 25 catalyst supports can be reused.

One process of leaching spent hydroprocessing catalysts is disclosed in U.S. Patent No. 4514368. An aqueous ammonia and ammonium salt leach solution is contacted with spent catalyst particles, which have previously been roasted in an oxygen-containing atmosphere, so as to remove therefrom nickel, cobalt, molybdenum and vanadium, the pH of the solution being kept at a value of at least 9.5.

30 French Patent Specification No. 972,178 discloses the ammoniacal leaching of nickel/cobalt containing laterite mineral which is simultaneously oxygenated to solubilise the nickel, the oxygenation being effected by means of oxygen or hydrogen peroxide as opposed to the previous use of air to effect the oxygenation.

It has now been found that when metal-containing particles comprising nickel and cobalt, which can be leached with an ammoniacal leaching solution containing ammonia and an ammonium salt and having a pH 35 of at least 9.5, are leached with a solution containing hydrogen peroxide at an initial concentration of from 0.02 to 0.2 M, then an unexpected significant increase in the amount of cobalt extracted relative to the amount of recovered nickel can be achieved.

Thus the invention has for its basis the use of hydrogen peroxide in the recovery of nickel and cobalt by the ammoniacal leaching of nickel/cobalt containing particles for the purpose of increasing the amount of 40 cobalt extracted relative to the amount of nickel extracted.

Thus in accordance with the present invention, there is provided a method of extracting cobalt, molybdenum, nickel and vanadium from spent catalyst particles containing said metals, wherein the metal-containing particles are roasted in an atmosphere containing molecular oxygen at a temperature in the range from 400 to 450° C and are thereafter leached for at least 15 minutes with an aqueous solution 45 containing ammonia and an ammonium salt and having a pH which is maintained at a value of at least 9.5, characterised in that the amount of cobalt and vanadium extracted from the particles is increased relative to the extracted nickel by incorporating into the aqueous solution hydrogen peroxide in an initial concentration of from 0.02 to 0.2 M.

Preferably, the initial pH of the aqueous leaching solution is at least 10.0, and more preferably, at least 50 10.4.

When the metal-containing particles are spent hydroprocessing catalyst particles containing carbon residue, the particles are first roasted in an atmosphere containing molecular oxygen at a temperature in the range from 400° to 450° C. The particles are then leached for at least 15 minutes with an aqueous solution containing ammonia, an ammonium salt, and hydrogen peroxide at a temperature of preferably from 50° C 55 to 95° C. The said aqueous solution preferably has an initial ammonia concentration of at least 2 M, and an initial ammonium salt concentration of at least 0.5M.

The roasting and leaching steps are repeated as needed to increase metals extraction.

The present invention can be used to recover metal values from metal-containing particles, such as

laterite or spent catalyst particles.

Laterite is a red, porous deposit containing large amounts of aluminum and ferric hydroxides, formed by the decomposition of certain rocks. Laterite often contains such metal values as nickel and cobalt. One method of removing the metal values from laterite is by leaching the laterite with ammoniacal ammonium carbonate solutions, but cobalt extraction is incomplete by these methods. By adding hydrogen peroxide to the leaching solution, and by having the solution at a pH of at least 9.5, preferably 10.4, we are able to significantly increase cobalt extraction.

The spent catalyst particles, as they come from the catalytic reaction vessel, are highly contaminated with carbonaceous deposits and sulfur. These contaminants are easily removed by combustion in an atmosphere containing molecular oxygen, for example, air, but, if the roasting temperature is too high, the amount of metals leached from the catalyst particles (particularly cobalt, nickel, and vanadium) tends to suffer. Suitable conditions for reaction with oxygen are from 400° C to 450° C. One method of controlling temperature is by diluting the oxygen with nitrogen. The catalyst so treated is free from substantial carbonaceous and sulfide residue and the metals contained therein can be easily removed by an aqueous ammonia leach.

The leach solution is an aqueous solution of $\text{NH}_3(\text{aq})$, hereinafter ammonia, $\text{NH}_4^+(\text{aq})$, hereinafter ammonium from a suitable ammonium salt, and hydrogen peroxide. Such a solution will be alkaline, which is preferred to solubilize vanadium and molybdenum, and will contain free ammonia, an effective complexing agent for nickel and cobalt. Ammonia/ammonium carbonate/ hydrogen peroxide solutions are especially well suited as they allow reagent recycle by means of distillation of the pregnant liquor and reabsorption in fresh or recycle aqueous solution. Ammonium sulfate is another preferred ammonium salt for the practice of this invention. Nickel and cobalt will be free cations and form $\text{M}(\text{NH}_3)_x^{++}$ where x is 3 to 6, hereinafter amine complexes, and molybdenum and vanadium will be in the form of oxyanions and will form ammonium salts.

The catalyst support of the spent catalyst particles will frequently be alumina. However, mixtures of alumina with other refractory inorganic oxides, for example, silica, boria, magnesia and titania, as well as supports that contain naturally occurring alumina-containing clays, for example, kaolin or halloysite, may be leached by the process of this invention.

In the buffered system used herein, two factors must be adjusted for optimal extraction: the concentration of ammonia, and the pH of the leach solutions. The solution must contain sufficient ammonia to complex the nickel and cobalt present. The pH throughout the reaction should be not lower than 9.5. Preferably, the initial pH (which is defined as the pH of the solution prior to contacting with the catalyst particles) is at least 10.0, more preferable at least 10.4.

Hydrogen peroxide significantly increases cobalt and vanadium extraction. The initial hydrogen peroxide concentration (which is defined as the hydrogen peroxide concentration of the solution prior to contacting with the catalyst particles) should be in the range of from 0.02 to 0.2 molar (M).

The initial ammonia concentration (which is defined as the ammonia concentration of the solution prior to contacting with the catalyst particles) should preferably be at least 2 M. The initial ammonium salt concentration (which is defined as the ammonium salt concentration of the solution prior to contacting with the catalyst particles) should preferably be at least 0.5 M.

The roasting step and the contacting step can be repeated as often as necessary to increase metals extraction.

The invention is illustrated by the following experimental example.

A two-level factorial design experiment was run to determine the effect of hydrogen peroxide and pH on spent catalyst leaching. The roasted catalyst feed analyzed 1.7% Co, 8.3% Mo, 1.4% Ni, and 4.5% V. Hydrogen peroxide concentrations were 0.02 M, 0.08 M, and 0.14 M; initial pH levels were 9.6, 10.0, and 10.4 (adjusted with aqueous ammonia). All combinations of these variables were tested and compared with a base-case leach at pH 10.0 which contained no peroxide. The leach conditions were 1 M $(\text{NH}_4)_2\text{CO}_3$ - 0.5 M $(\text{NH}_4)_2\text{SO}_4$; 5% solids, 80° C, three hours.

The results of Table I clearly show that cobalt extraction increased with increasing pH and hydrogen peroxide concentration. The effects of either variable are especially pronounced at low pH or low peroxide concentration. Toward the higher range of both variables, cobalt extraction averages about 78% compared with 51% for the base case without peroxide.

Vanadium extraction was remarkably insensitive to the combination of variables tested. Still, the consistent 88% extraction was a considerable increase over the 78% observed in the base case. We attribute the increased vanadium and cobalt extraction to the formation of peroxo complexes.

Molybdenum and nickel extractions were not enhanced by peroxide addition. However nickel extraction did seem to decrease slightly with peroxide, but at higher pH values, extraction returned to base-case levels of about 80%. Molybdenum extraction was quite steady at about 93%.

TABLE I

EFFECT OF HYDROGEN PEROXIDE AND PH ON METALS EXTRACTED FROM SPENT CATALYSTS							
Test	Initial pH	Equilibrium pH	[H ₂ O ₂] Molar	Metals Extraction, %			
				Co	Mo	Ni	V
1	10.00	9.75	0.00	51.3	91.8	81.1	78.3
2	9.60	9.42	0.02	60.6	92.5	70.5	88.1
3	9.60	9.44	0.08	66.6	92.3	67.4	86.6
4	9.60	9.47	0.14	80.2	94.3	76.2	90.6
5	10.00	9.70	0.02	69.3	92.7	76.9	88.0
6	10.00	9.77	0.08	78.2	93.6	76.4	89.4
7	10.00	9.73	0.08	75.9	93.4	76.2	87.6
8	10.00	9.78	0.14	75.9	93.4	72.4	88.1
9	10.40	9.97	0.02	72.6	93.0	82.5	88.2
10	10.40	9.78	0.08	81.6	93.6	80.8	88.5
11	10.40	9.81	0.14	78.8	93.6	79.8	88.4

Claims

1. A method of extracting cobalt, molybdenum, nickel and vanadium from spent catalyst particles containing said metals, wherein the metal-containing particles are roasted in an atmosphere containing molecular oxygen at a temperature in the range from 400 to 450° C and are thereafter leached for at least 15 minutes with an aqueous solution containing ammonia and an ammonium salt and having a pH which is maintained at a value of at least 9.5, characterised in that the amount of cobalt and vanadium extracted from the particles is increased relative to the extracted nickel by incorporating into the aqueous solution hydrogen peroxide in an initial concentration of from 0.02 to 0.2 M.
2. A method according to Claim 1, wherein the roasting and leaching steps are repeated to increase metals extraction.
3. A method according to Claim 1 or 2, wherein the leaching step is carried out at a temperature of from 50 to 95° C.
4. A method according to any preceding claim, wherein said aqueous solution has an initial ammonia concentration of at least 2 M and an initial ammonium salt concentration of at least 0.5 M.
5. A method according to any preceding claim, wherein said initial pH is at least 10.0.
6. A method according to Claim 4, wherein said initial pH is at least 10.4.

Revendications

1. Procédé pour extraire le cobalt, le molybdène, le nickel et le vanadium de particules d'un catalyseur usé contenant lesdits métaux, dans lequel les particules métallifères sont calcinées dans une atmosphère contenant de l'oxygène moléculaire à une température comprise dans la plage de 400 à 450° C et sont ensuite lixiviées pendant au moins 15 minutes avec une solution aqueuse contenant de l'ammoniac et un sel d'ammonium et ayant un PH qui est maintenu à une valeur d'au moins 9,5, caractérisé en ce que la quantité de cobalt et de vanadium extraite des particules est élevée par rapport au nickel extrait par l'incorporation, dans la solution aqueuse, de peroxyde d'hydrogène à une concentration initiale de 0,02 à 0,2 M.
2. Procédé suivant la revendication 1, dans lequel les étapes de calcination et de lixiviation sont répétées afin d'accroître l'extraction des métaux.
3. Procédé suivant la revendication 1 ou 2, dans lequel l'étape de lixiviation est conduite à une

température de 50 à 95° C.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la solution aqueuse a une concentration initiale en ammoniac d'au moins 2 M et une concentration initiale en sel d'ammonium d'au moins 0,5 M.
5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le pH initial est d'au moins 10,0.
6. Procédé suivant la revendication 4, dans lequel le pH initial est d'au moins 10,4.

Patentansprüche

1. Verfahren zum Extrahieren von Kobalt, Molybdän, Nickel und Vanadium aus verbrauchten, diese Metalle enthaltenden Katalysatorteilchen, bei dem die Metall-enthaltenden Teilchen in einer molekularen Sauerstoff enthaltenden Atmosphäre bei einer Temperatur im Bereich von 400 bis 450° C geröstet und danach mindestens 15 Minuten mit einer wässrigen Lösung gelaugt werden, die Ammoniak und ein Ammoniumsalz enthält und einen pH aufweist, der bei einem Wert von mindestens 9,5 gehalten wird, dadurch gekennzeichnet, daß die Menge des aus den Teilchen extrahierten Kobalts und Vanadiums relativ zu der Menge des extrahierten Nickels zunimmt, wenn Wasserstoffperoxid in einer Ausgangskonzentration von 0,02 bis 0,2 M der wässrigen Lösung zugegeben wird.
2. Verfahren nach Anspruch 1 bei dem die Röst- und Laugungsschritte zur Erhöhung der Metallextraktion wiederholt werden.
3. Verfahren nach Anspruch 1 oder 2, bei dem der Laugungsschritt bei einer Temperatur von 50 bis 95° C durchgeführt wird.
4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die wässrige Lösung eine Ammoniakausgangskonzentration von mindestens 2 M und eine Ammoniumsalzausgangskonzentration von mindestens 0,5 M hat.
5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem der Ausgangs-pH mindestens 10,0 ist.
6. Verfahren nach Anspruch 4, bei dem der Ausgangs-pH mindestens 10,4 ist.